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(54) **COMPOSITIONS POUR REVETEMENT POLYMERISABLES AUX UV, CONTENANT DES URETHANE-(METH)ACRYLATES ET DES GROUPES ISOCYANATES LIBRES**

(54) **UV-CURABLE COATING COMPOSITIONS CONTAINING URETHANE-(METH)ACRYLATES WITH FREE ISOCYANATE GROUPS**

(57)

The present invention relates to coating compositions containing a) a urethane-(meth)acrylate containing; (meth)acryloyl groups and free isocyanate groups, b) optionally a polyisocyanate other than a), c) a UV initiator which initiates free radical polymerization and d) a compound containing isocyanate-reactive groups. The present invention also relates to a process for preparing a coating from this coating composition.



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UV-CURABLE COATING COMPOSITIONS CONTAINING URETHANE-(METH)ACRYLATES WITH FREE ISOCYANATE GROUPS

ABSTRACT OF THE DISCLOSURE

The present invention relates to coating compositions containing

- a) a urethane-(meth)acrylate containing (meth)acryloyl groups and free isocyanate groups,
- b) optionally a polyisocyanate other than a),
- c) a UV initiator which initiates free radical polymerization and
- d) a compound containing isocyanate-reactive groups.

The present invention also relates to a process for preparing a coating from this coating composition.

UV-CURABLE COATING COMPOSITIONS CONTAINING URETHANE-(METH)ACRYLATES WITH FREE ISOCYANATE GROUPS

BACKGROUND OF THE INVENTION

5 **Field of the Invention**

The present invention relates to coating compositions containing urethane-(meth)-acrylates having free isocyanate groups and compounds containing isocyanate-reactive groups and to a process for preparing coatings from these coating compositions by a dual cure mechanism.

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Description of the Prior Art

The curing of coating compositions containing (meth)acryloyl groups by UV-initiated free radical polymerization is known and used industrially. It is one of the fastest curing methods in coating technology. However, coatings cured throughout with UV have disadvantages, such as high volume shrinkage, which can lead to adhesion problems. The high crosslinking density inherent to the system leads to brittleness, a lack of elasticity and a lack of impact resistance. Also, complete curing of UV-curable coating compositions containing (meth)acryloyl groups requires the availability of an adequate radiation dose of appropriate wavelength. Poorly exposed regions cure to a reduced extent, which leads to considerable losses in the surface resistance, and non-exposed regions do not cure at all.

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Coatings based on polyisocyanates and compounds containing isocyanate-reactive groups, preferably polyols or sterically hindered polyamines, can be formulated to obtain a wide range of properties, such as adhesion, elasticity, impact resistance and stability to weathering, based on the choice of reaction partners. However, compared with radiation-curing compositions, complete curing requires a long time and preferably high temperatures, but does not require the presence of a special light source.

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Combinations of the two types of curing are also known, e.g., as dual cure systems. US-A 4,342,793 describes compositions containing a saturated polyol, a polyiso-

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cyanate and a radiation-curable reactive diluent, i.e., low molecular weight acrylic acid esters. Curing is carried out by irradiation in order to polymerize the reactive diluent and thereafter by thermal curing to form a polyurethane from the polyol and the polyisocyanate.

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The disadvantage of such systems is that under adverse irradiation, non-incorporated reactive diluent can remain in the cured paint film. Because of its potential extractability, this can lead to physiological problems on skin contact with the paint film. In addition, it adversely influences properties of the paint film, such as hardness and physical and chemical resistance.

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An object of the present invention is to provide a coating composition that may be rapidly cured by UV to allow handling of the coated substrates and that may be crosslinked by the reaction of NCO groups with compounds containing isocyanate-reactive groups, preferably polyols and/or sterically hindered polyamines, to allow the properties to be adjusted according to the intended use and to provide adequate curing even on non-exposed or poorly exposed regions.

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Surprisingly, it has been found that this object may be achieved with the coating compositions according to the present invention, which contain polyols, urethane-(meth)acrylates having (meth)acryloyl groups and free NCO groups and optionally other polyisocyanates. After UV curing the resulting coatings are dry, such that they can be handled, and may be crosslinked to completion by the reaction of NCO groups to obtain coatings having high chemical and mechanical resistance. In the event of poor exposure during UV cure, which causes a certain residual double bond density, crosslinking via reaction of the NCO groups guarantees the minimum required resistance level.

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These results are surprising since it was expected that the two reaction processes would hinder each other and that the rapid UV-initiated polymerization would virtually "freeze" the significantly slower reaction of the NCO groups such that they

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no longer react with isocyanate-reactive groups.

SUMMARY OF THE INVENTION

The present invention relates to coating compositions containing

- 5 a) a urethane-(meth)acrylate containing (meth)acryloyl groups and free isocyanate groups,
- b) optionally a polyisocyanate other than a),
- c) a UV initiator which initiates free radical polymerization and
- 10 d) a compound containing isocyanate-reactive groups.

The present invention also relates to a process for preparing a coating from this coating composition.

DETAILED DESCRIPTION OF THE INVENTION

- 15 The present coating composition is preferably prepared in two components, component I) containing components a)+b) and component II) containing components c)+d).

To achieve stability to weathering

- 20 e) a UV absorber having an absorption range up to a maximum of 390 nm and
 - f) a HALS stabilizer
- may optionally be added to component II). In addition,
- g) conventional paint additives, such as flow control or deaerating agents and
 - h) catalysts to accelerate the reaction of NCO

- 25 may optionally be added to component II).

For reduce the viscosity, components I) and II) can each contain a solvent which is inert to the polyisocyanate addition reaction.

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Components I) and II are combined such that the equivalent ratio of NCO groups to

isocyanate-reactive groups is 2:1 to 0.8:1, preferably 1.2:1 to 0.8:1 and more preferably 1:1.

5 Compounds a) are prepared from monohydric alcohols containing (meth)acryloyl groups and di- or polyisocyanates. Preparation processes for urethane-(meth)acrylates are known and described, e.g. in DE-A 16 44 798, DE-A 21 15 373 (U.S. Patent 3,782,961), DE-A 27 37 406 (U.S. Patent 4,225,695). To ensure that the urethane-methacrylates according to the invention contain free isocyanate groups, the di- or polyisocyanates are reacted with the monohydric alcohols an equivalent ratio
10 of NCO groups to OH groups of 1:0.2 to 1:0.8, preferably 1:0.3 to 1:0.6.

Monohydric alcohols containing (meth)acryloyl groups include esters containing a free hydroxyl group and based on the reaction product of acrylic acid or methacrylic acid with dihydric alcohols, such as 2-hydroxyethyl, 2- or 3-hydroxypropyl or 2-, 3-
15 or 4-hydroxybutyl (meth)acrylate, and any mixtures thereof. Also suitable are monohydric alcohols containing (meth)acryloyl groups or reaction products containing these alcohols, which are obtained by esterification of an n-hydric alcohol or a mixture of these alcohols with (meth)acrylic acid wherein n has a value of 2 to 4, preferably 3. To prepare these alcohols, n - 0.8 to n - 1.2 moles, preferably n - 1
20 moles of (meth)acrylic acid are reacted for mole of n-hydric alcohol.

Examples of these compounds include the reaction products of i) glycerol, trimethylolpropane, pentaerythritol, low molecular weight alkoxylation products of these alcohols (such as ethoxylated or propoxylated trimethylolpropane or the addition product of ethylene oxide onto trimethylolpropane, e.g., one having an OH
25 number 550), and mixtures of least trihydric alcohols with dihydric alcohols (such as ethylene glycol or propylene glycol), with ii) (meth)acrylic acid in the previously described molar ratios.

30 These compounds have a number average molecular weight (M_n) of 116 to 1,000, preferably 116 to 750 and more preferably 116 to 158.

Suitable di- or polyisocyanates include the known di- or polyisocyanates, preferably those containing (cyclo)aliphatically-bound isocyanate groups, such as butylene diisocyanate, hexamethylene diisocyanate, 2,2,4- and/or 2,4,4-trimethyl-hexamethylene diisocyanate, neopentyl diisocyanate, isophorone diisocyanate, dicyclohexylmethane diisocyanate and derivatives thereof containing urethane, allophanate, isocyanurate, biuret and/or uretdione groups. Diisocyanates containing urethane groups obtained from diisocyanates and dihydric alcohols are also suitable.

10 The addition reaction to prepare component a) can be accelerated in known manner with suitable catalysts, such as tin octoate, dibutyltin dilaurate or tertiary amines.

The resulting urethane-(meth)acrylates containing free NCO groups must be stabilized against premature polymerization by the addition of suitable inhibitors and antioxidants, such as phenols, hydroquinones and quinones, such as e.g. 2,5-di-tert-butylquinone. These inhibitors are added during or after preparation in an amount of 0.001 to 0.3 wt.%, based on the weight of the reactants. The products can be prepared in solvents which are inert to the preparation reaction and to the subsequent curing reaction.

20 Optional polyisocyanates b) include polyisocyanates other than those set forth under a), i.e., those that do not contain (meth)acrylate groups. Preferably, they are selected from polyisocyanates that contain isocyanurate, allophanate, biuret and/or uretdione groups, more preferably polyisocyanates of this type that are prepared from hexamethylene diisocyanate, 2,2,4- and/or 2,4,4-trimethyl-hexamethylene diisocyanate or isophorone diisocyanate.

30 UV initiators c) include 2-hydroxyphenyl ketones such as 1-hydroxy-cyclohexyl phenyl ketone, benzyl ketals such as benzyl dimethyl ketal, acylphosphine oxides such as bis-(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, benzophenone and derivatives thereof and mixtures of the preceding UV initiators.

Compounds d), which contain isocyanate-reactive groups, include polyols, such as polyester, polyacrylate polyols and polyether polyols, and compounds containing sterically hindered amino groups. The polyesters can be obtained by the esterification of di- or triols with dicarboxylic acids. The polyacrylate polyols may be prepared by the copolymerization of unsaturated monomers, preferably mixtures containing (meth)acrylic acid esters, hydroxyalkyl(meth)acrylic acid esters and optionally styrene and/or other monomers, such as acrylonitrile. The polyether polyols include those obtained by the alkoxylation of diols and/or polyols. The compounds containing sterically hindered amines are obtained by the addition of maleic acid esters onto (cyclo)aliphatic primary diamines as disclosed in U.S. Patent 5,126,170 and 5,236,741.

To stabilize the cured coating to weathering, a UV absorber having an absorption range up to a maximum of 390 nm and a HALS stabilizer can preferably be added to component II). Suitable UV absorbers include those of the triphenyltriazine type, e.g., Tinuvin 400 (Ciba), or those of the oxalic acid dianilide type, e.g., Sanduvor 3206 (Clariant). The UV absorbers are preferably added in amounts of 0.5 to 3.5%, based on resin solids.

Suitable HALS stabilizers include those that are commercially available, such as Tinuvin 292 or Tinuvin 123 (Ciba) or Sanduvor 3058 (Clariant). These HALS stabilizers are preferably added in amounts of 0.5 to 2.5%, based on resin solids.

Suitable additives g) include deaerating agents, such as polyacrylates, and flow control agents, such as polysiloxanes.

Suitable solvents are those which are inert towards isocyanate groups and C=C double bonds, such as esters, ketones, ethers, ether-esters, alkanes, and aromatic solvents, e.g., xylenes or toluene.

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If all of the components of the coating composition according to the invention are formulated as a one-component composition, the system has a limited pot life. A preferred formulation is a two-component composition in which component I) contains components a) and b) and component II) contains components c) and d) and optionally components e) to h). The two-component compositions have a storage stability that corresponds to the stability of the individual components. Components I) and II) are mixed in the required ratio before application, or are applied via so-called two-component units.

The coating compositions according to the invention can preferably be applied by a spraying, pouring or rolling application. Complete curing can be carried out:

1. by optionally allowing added solvents to evaporate at room temperature or at elevated temperature, preferably up to 80°C;
2. by UV curing using, e.g., commercially available high or medium pressure mercury lamps, which can be doped with other elements and preferably have an output of 80 to 240 W/cm lamp length; and
3. by reacting (crosslinking) the NCO-containing compounds with the isocyanate-reactive components at room temperature or at elevated temperatures, preferably up to 150°C.

A preferred complete curing process is one in which the reaction of the NCO-containing compounds proceeds partly during UV curing at an elevated temperature (10°C to 50°C above reaction temperature) or during a longer UV irradiation time (exposure time) at an unchanged temperature.

EXAMPLES

Example 1 - Preparation of a urethane-acrylate containing isocyanate groups according to the invention:

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1,268.7 g of an HDI-isocyanurate having an NCO content of 23%, 383.9 g of methoxypropyl acetate, 0.96 g of dibutyltin dilaurate and 1.92 g of 2,6-di-tert-butylcresol were weighed into a stirred tank equipped with a thermoelement, dropping funnel, reflux condenser, gas feed line and gas removal line. While stirring, three times the
10 tank volume of air per hour was passed through and six times the tank volume of nitrogen per hour was passed over the mixture, which was then heated to 50°C. 266.8 g of hydroxyethyl acrylate were added dropwise such that the temperature was increased to a maximum of 60°C due to the exothermic reaction. After 6 to 8 hours when the addition of the hydroxyethyl acrylate was complete, the mixture was
15 subsequently stirred at 60°C for a further hour. A urethane-acrylate solution having an NCO content of 9.2% and a viscosity of 1,070 mPa.s (23°C) was formed.

Example 2 - Preparation, application and testing of a coating composition according to the invention

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A coating composition was prepared from components I) and II) at an equivalent ratio of OH to NCO of 1.0:1.0.

Component 1: the urethane-acrylate solution from Example 1
25 Component 2: a polyacrylate polyol having an OH content of 3% and present as a 70% solution in butyl acetate (Desmophen A VP LS 2009/1, Bayer AG), also containing 1%, based on resin solids, of a HALS stabilizer (Sanduvor 3058, Clariant); 2.5%, based on resin solids, of a UV absorber (Sanduvor 3206, Clariant); and 5%, based on the
30 solids content of component 1), of Irgacure 184 Photoinitiator (Ciba)

For application the mixture was diluted to a solids content of 30% with methoxypropyl acetate and applied in an amount sufficient to obtain a film thickness of approx. 120 g/m² using a 1.5 mm nozzle under 3 bar to a metal plate precoated with a pigmented 2-component polyurethane coating.

The wet films were cured by 3 different methods:

2a) 30 min, 130°C

2b) 10 min, 60°C; UV curing (1m/min belt speed, 1 high pressure Hg lamp 80 W/cm, 10 cm lamp distance); and 30 min, 130°C

2c) 10 min, 60°C; UV curing as in 2b); after-curing at room temperature

The resulting hardness of the coatings was tested by pendulum damping by the König method, and the resistance to solvents and to 1% sulphuric acid were tested.

The following table sets forth the results.

Curing method	2a		2b		2c	
Pendulum damping by the König method, sec	71		140		90 after 30 min 110 after 1 d 120 after 2 d 140 after 7 d storage at room temperature	
Solvent resistance	Action time		Action time		Action time	
	1 min	5 min	1 min	5 min	1 min	5 min
Xylene	2	3	0	0	0*	0*
Methoxypropyl acetate	2	3	0	0	0*	0*
Ethyl acetate	3	3	0	2	0*	0*
Acetone	3	3	1	3	1*	2*
Resistance to 1% H ₂ SO ₄ , first damage (brown edge) at	36°C		46°C		46°C	

* Condition after storage at room temperature for 7 d

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The numbers for solvent resistance denote:

0 = unchanged

1 = trace of a change

2 = slightly changed

5 3 = moderately changed

4 = greatly changed

5 = dissolved/destroyed

10 Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:-

1. A coating composition comprising
 - a) a urethane-(meth)acrylate containing (meth)acryloyl groups and free isocyanate groups,
 - b) optionally a polyisocyanate other than a),
 - c) a UV initiator which initiates free radical polymerization and
 - d) a compound containing isocyanate-reactive groups.
2. The coating composition of Claim 1 wherein the coating composition is a two-component composition in which the first component contains components a) and b) and the second component contains components c)+d).
3. The coating composition of Claim 1 wherein the urethane-meth)acrylate is the reaction product of a monohydric alcohol containing a (meth)acryloyl group with a polyisocyanate at an equivalent ratio of NCO groups to OH groups of 1:0.2 to 1:0.8.
4. The coating composition of Claim 2 wherein the urethane-meth)acrylate is the reaction product of a monohydric alcohol containing a (meth)acryloyl group with a polyisocyanate at an equivalent ratio of NCO groups to OH groups of 1:0.2 to 1:0.8.
5. The coating compositions of Claim 1 wherein component c) comprises a polyol.
6. The coating compositions of Claim 2 wherein component c) comprises a polyol.
7. The coating compositions of Claim 3 wherein component c) comprises a polyol.

8. The coating compositions of Claim 4 wherein component c) comprises a polyol.
- 5 9. The coating composition of Claim 1 wherein component c) comprises a polyfunctional sterically hindered secondary amine.
- 10 10. The coating composition of Claim 2 wherein component c) comprises a polyfunctional sterically hindered secondary amine.
- 11 11. The coating composition of Claim 3 wherein component c) comprises a polyfunctional sterically hindered secondary amine.
- 15 12. The coating composition of Claim 4 wherein component c) comprises a polyfunctional sterically hindered secondary amine.
- 13 13. The coating compositions of Claim 1 which further comprises a UV absorber having an absorption range of up to 390 nm.
- 20 14. The coating composition of Claim 1 which further comprises a HALS amine.
- 15 15. The coating composition of Claim 14 which further comprises a HALS amine.
- 25 16. A process for the production of coatings which comprises coating a substrate with the coating composition of Claim 1 and curing the coating by UV-initiated free radical polymerization and subsequently by the reaction of NCO groups with isocyanate-reactive groups.